



# Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions

A. Marcilla\*, M.I. Beltrán, R. Navarro

Departamento Ingeniería Química, Facultad de Ciencias, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain

## ARTICLE INFO

### Article history:

Received 7 May 2008

Received in revised form 15 July 2008

Accepted 24 July 2008

Available online 9 August 2008

### Keywords:

Batch reactor

Thermal pyrolysis

Catalytic pyrolysis

LDPE

HDPE

HZSM5

HUSY

## ABSTRACT

The thermal and catalytic pyrolysis of LDPE and HDPE over HZSM5 and HUSY have been studied under dynamic conditions in a batch reactor. The products evolved have been analyzed, and results have been compared with those found in the bibliography. Particular attention was paid to any coincidences and differences encountered. The yields of gases, liquids and waxes for all the systems employed are presented, along with the composition of each fraction. The general carbon number distribution is shown, as well as the carbon number distribution for the main compounds present in the gaseous and the liquid fractions. Finally, the 10 major compounds obtained for each system are described.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

In 2003, Western Europe consumed 39,706,000 tonnes of plastic, whilst only 21,150,000 tonnes of plastic was collected as waste that year. These quantities are increasing at 2.3% a year [1]. Among the various plastic waste recycling methods, feedstock recycling is becoming a promising alternative for recovering valuable gasoline-range hydrocarbons.

Polyolefins constitute 68% of all plastic wastes. Thermal degradation of polyolefins produces a whole spectrum of hydrocarbons, including paraffins, olefins and aromatics. For polyethylene, the main polymeric component of municipal plastic wastes along with polypropylene, pyrolysis occurs by a random-chain scission mechanism, which involves several steps, such as initiation, propagation and/or free-radical transfer, and termination. While propagation reactions yield the monomer, free radical transfer reactions, instead, provoke hydrogen abstraction from a polymer chain, resulting in the formation of one saturated end, one unsaturated end and another new free radical [2,3]. Depending on the experimental conditions, intra- or intermolecular hydrogen transfer is favoured, leading to an increase in the production of olefins and diolefins in the first case, or paraffins in the latter [4].

Either way, a large number of paraffinic and olefinic compounds will have been obtained by the end of the polyethylene thermal degradation [5].

Catalytic degradation of polymer wastes has been extensively investigated to improve gasoline yield. During catalytic pyrolysis, the solid polymer melts and disperses around the catalyst. The molten polymer is drawn into the spaces between particles and hence to active sites at the external surface of the catalyst. Surface reaction produces low molecular weight materials which, if sufficiently volatile at reaction temperature, can either diffuse through the polymer film, as products, or react further in the pores [6]. These reactions proceed via carbocations as transition states. The reaction rate is governed by both the nature of the carbocation formed, and the nature and strength of the acid site involved in the catalysis [7,8]. Carbocations are formed in reactions that can be grouped into four main types: (1) the addition of a cation to an unsaturated molecule, (2) the addition of a proton to a saturated molecule, (3) the removal of an electron from an electrically neutral species, and (4) heterolytic fission of a molecule. Regardless of the origin of the carbocation, once it is formed it may undergo any of the following processes: (1) charge isomerization, (2) chain isomerization, (3) hydride transfer, (4) alkyl transfer, and (5) formation and breaking of carbon–carbon bonds. As a result of this complex process, product distributions reflect features of the catalysts in relation to their pore systems and chemical composition [6]. The carbon atom number distribution of products obtained under

\* Corresponding author. Tel.: +34 96 590 3400x3789; fax: +34 96 590 3826.  
E-mail address: antonio.marcilla@ua.es (A. Marcilla).

catalytic conditions is, in general, narrower compared to the distribution obtained by thermal degradation.

The objective of the present study has been to analyze the effect of catalyst and polymer structure on the products obtained by thermal and catalytic pyrolysis of LDPE and HDPE over HZSM5 and HUSY zeolites, focusing on the composition of gas and liquid fractions, variations with the carbon number and the compound type, and on the yields of the most important compounds obtained in each system. A detailed comparison is made with results obtained by other authors under similar or different experimental conditions that may contribute to a better understanding of the potential of the catalytic pyrolysis process as a promising polyethylene recycling process.

## 2. Experimental

### 2.1. Materials

Two commercial polyethylene samples were used in this study: low density polyethylene (LDPE 780R supplied by DOW Chemical) and high density polyethylene (HDPE HD3560UR supplied by BP). Both polymers were supplied in powder form with a maximum particle size of 500 µm. The melt flow index (MFI) determined for LDPE and HDPE was 20 and  $6 \text{ g} \times 10 \text{ min}^{-1}$ , respectively. MFI was measured as the quantity of polymer extruded in 10 min through a 1 mm die at 190 °C, under a weight of 2.16 kg. Density was determined at room temperature, and is mainly related to crystallinity which, in turn, is related to degree of branching. The density was 0.923 and 0.935 g cm<sup>-3</sup> for LDPE and HDPE, respectively.

Two different commercial zeolites were chosen: HZSM5 and HUSY, both provided by GRACE-Davison. Although both zeolites are microporous catalysts, they exhibit very different properties. In fact, HZSM5 is a zeolite with two types of channels: zig-zag ( $5.1 \text{ \AA} \times 5.5 \text{ \AA}$ ) and linear ( $5.3 \text{ \AA} \times 5.6 \text{ \AA}$ ), whereas HUSY contains supercages (12 Å) that are tetrahedrally connected by 12-membered ring windows having a diameter of 7.4 Å each. HZSM5 has a particle size of 3 µm, a BET surface area of 341 m<sup>2</sup> g<sup>-1</sup> and a micropore volume of 0.16 cm<sup>3</sup> g<sup>-1</sup>, whilst for HUSY, the corresponding values are 1 µm, 614 m<sup>2</sup> g<sup>-1</sup> and 0.29 cm<sup>3</sup> g<sup>-1</sup>, respectively. Data obtained from temperature programmed desorption

(TPD) of ammonia indicate that HZSM5 has two types of acid sites: weak acid sites, for which maximum desorption of ammonia occurs at 166 °C (1.15 mmol NH<sub>3</sub> g<sup>-1</sup>), and strong acid sites, with a desorption temperature of 416 °C (0.88 mmol NH<sub>3</sub> g<sup>-1</sup>). HUSY, on the other hand, exhibits a single, very broad peak centred at 154 °C having an ammonia desorption of 2.12 mmol NH<sub>3</sub> g<sup>-1</sup>.

### 2.2. Equipment and experimental procedure

A batch reactor was used to carry out the degradation of polyethylene. A diagram of the reactor employed is shown in Fig. 1. The reactor was in an upright position. This disposition and the carrier gas inlet at the bottom of the reactor facilitated the exit of the gas generated through the outlet at the top. The reactor outlet was heated to 300 °C to prevent condensation. The reactor was heated by an electric furnace, which was connected to a programmable temperature controller. Around 600 mg of sample was placed in a crucible which was leaned against a rod in the middle of the reactor. A thermocouple in direct contact with the sample was used to monitor the actual temperature of the process. In catalytic experiments, the catalyst to polymer ratio was 1/10. Prior to the experiment, the system was purged for 30 min with a nitrogen stream at room temperature to ensure an inert atmosphere. The nitrogen flow rate used was 150 mL min<sup>-1</sup> (STP) and was maintained during the whole pyrolysis process. Experiments were carried out from 30 to 550 °C at 5 °C min<sup>-1</sup>. Under these conditions, all the polymer was converted to gaseous, liquid and waxy products, and no solid residue, apart from the coke deposited on the catalyst, was observed after each experiment. Condensable products were collected in two cooling traps, filled with stainless steel Dixon rings, placed in an ice/NaCl bath, whilst gaseous products were collected in a 10 L valved Tedlar bag.

### 2.3. Analysis of products

#### 2.3.1. Gaseous compounds

The amount of gas contained within each of the bags was determined as the volume of water displaced in an inverted column, assuming ideal gas behaviour since the gas is mostly composed of a known quantity of nitrogen. The compounds contained in the gas were analyzed by an Agilent 6890N gas

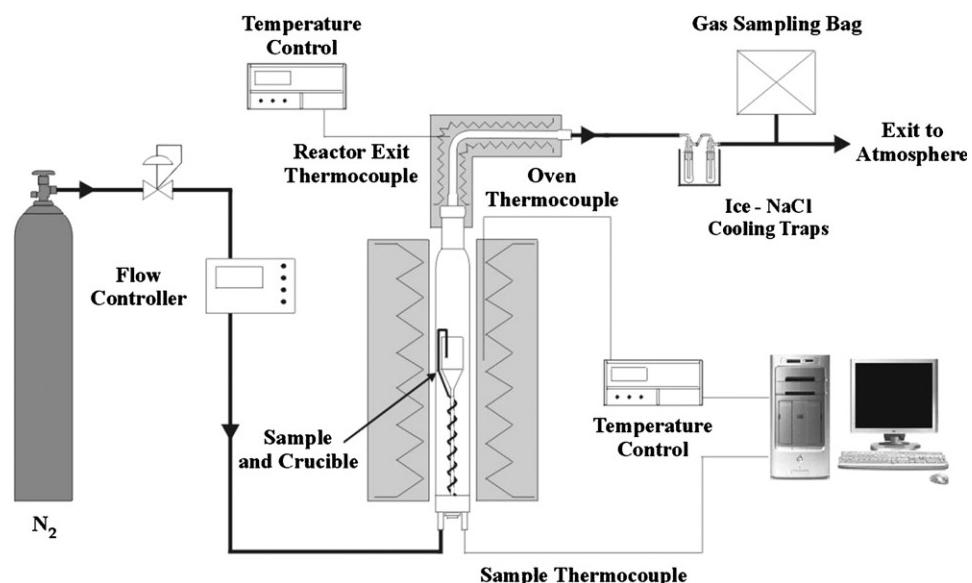


Fig. 1. Schematic diagram of the batch reactor system.

chromatograph (GC) equipped with a flame ionization detector (FID), using a GS-Alumina column ( $30\text{ m} \times 0.53\text{ mm ID}$ ). Standard gaseous hydrocarbons (from Scott Specialty Gases) were used to identify and quantify the volatile compounds. Compounds corresponding to chromatographic peaks that could not be identified with standards were analyzed by a gas chromatograph coupled to a mass spectrometer (GC-MS) (Agilent 6890N GC-MSD 5973N), using a GS-GasPro column ( $30\text{ m} \times 0.32\text{ mm ID}$ ).

### 2.3.2. Liquid-waxes compounds

Condensable products were trapped in stainless steel Dixon rings inside cooling traps. The amount of liquid generated was determined as the difference in weight of the traps after and before the experiment. The reactor and all conduits were also weighed before and after experiments to make sure that no condensable products had deposited on their interior surfaces, and they were washed with *n*-hexane to collect the liquid fraction. Subsequently, liquid fractions were analyzed by a gas chromatograph coupled to a mass spectrometer (GC-MS) (Agilent 6890N GC-MSD 5973N), using a HP-5MS column ( $30\text{ m} \times 0.25\text{ mm ID}$ ).

### 2.3.3. Catalyst residue

The amount of coke deposited on the zeolite residues was measured in a Mettler Toledo thermobalance (TGA/SDTA851e/LF/1600). Dynamic experiments were carried out from 30 to  $900\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C min}^{-1}$  under oxygen atmosphere ( $30\text{ mL min}^{-1}$  STP). The coke deposited on the zeolite is expressed as mg per 100 mg of polyethylene.

## 3. Results and discussion

### 3.1. Global yields

#### 3.1.1. Thermal pyrolysis

**Table 1** shows the yields of gases, condensable products (liquids and waxes) and coke for the thermal pyrolysis of LDPE and HDPE, and for the catalytic processes over HZSM5 and HUSY. In order to check the reproducibility of the experiments, all the processes were repeated. The missing or excess 10% in material balances can be attributed mainly to errors in the determination of the amount of gases generated, or to the condensation of some products on reactor walls. The components of each fraction were grouped into *n*-paraffins, *iso*-paraffins, 1-olefins, olefins (as different from 1-olefins and including alkynes and dienes) and aromatics. **Table 2** shows the weight fraction of each group.

As can be seen, condensable products were by far the major fraction for the thermal processes, and no coke deposits were observed (**Table 1**). In both fractions (gas and liquid/wax) 1-olefins were the main components, followed by *n*-paraffins and other olefins (**Table 2**). Only small quantities of *iso*-paraffins and aromatics were detected in the gas, but none were found in the liquid/wax fraction.

A glance at the bibliography shows a wide divergence in results obtained by different authors in relation to the yield of gases and liquids/waxes, and the composition of each fraction. The type of

reactor and the experimental conditions employed in each study may account for the observed discrepancy. Hernández et al. [9,10] studied the thermal pyrolysis of HDPE in a fluidized bed reactor at different temperatures. These authors described an increase in the yield of gases when the temperature was increased from 400 to  $800\text{ }^{\circ}\text{C}$ . The main components in the gases were 1-olefins, whilst in the liquid fraction the composition was strongly dependent on the temperature; *n*-paraffins were found more frequently at low temperatures and 1-olefins at high temperatures. These results were highly concordant with those obtained by Williams and Williams [11], who also carried out the pyrolysis of LDPE in a fluidized bed reactor, and in the same range of temperatures. On the other hand, Predel and Kaminsky [12] reported olefins as the major components of both the gas and liquid fractions, for the pyrolysis of polyethylene at  $530\text{ }^{\circ}\text{C}$  in the same type of reactor. The difficulty in avoiding secondary reactions using a fluidized bed reactor has been described [13], and would justify the differences found among these authors.

In other studies on polyethylene pyrolysis, carried out in batch reactors such as the one employed for our experiments, the divergence in results reported by the various authors is even greater. In this type of reactor, the extent to which secondary reactions proceed is not as great as in fluidized bed reactors, but heat transfer is not as well favoured, and consequently, other factors, such as the sample quantity and size, or the flow rate of the carrier gas, can be determining. Ballice et al. [14] (heating rate  $2\text{ }^{\circ}\text{C min}^{-1}$ ; HDPE and LDPE pellets mixed with sand;  $90\text{ mL min}^{-1}$  argon; the amount of polymer is not mentioned, but is presumably high according to the reactor size and the amount of sand employed) found that conversion to gases was 44%, and also noted a higher rate of formation of *n*-paraffins compared to 1-olefins. These results differ substantially from those in **Tables 1** and **2**. Nevertheless, Seo et al. [15] (heating rate  $5\text{--}8\text{ }^{\circ}\text{C min}^{-1}$ ; HDPE pellets, no data on carrier gas supplied) reported very similar results to those presented here; gases and liquids/waxes yielded in 13 and 84%, respectively. The *n*-paraffins and 1-olefins formed in nearly equal quantities (40.5 and 39.9 wt%, respectively). A comparable proportion of paraffins and olefins has been also referenced by Aguado et al. [16] (heating rate  $10\text{ }^{\circ}\text{C min}^{-1}$ ;  $5.0\text{ g}$  of LDPE pellets;  $39.0\text{ mL min}^{-1}$  nitrogen). Williams and Williams [17] (heating rate  $25\text{ }^{\circ}\text{C min}^{-1}$ ;  $200\text{ mL min}^{-1}$  nitrogen) obtained results that match those presented here: 15.0 and 84.3% gases and liquids/waxes yielded for LDPE, respectively, and 16.8 and 79.7% for HDPE. In their study, a much higher percentage of olefins formed compared to paraffins.

Regarding the influence of the type of polyethylene on the thermal pyrolysis, LDPE and HDPE behave very similarly according to **Tables 1** and **2**. The only remarkable difference resides in the proportion of 1-olefins, which is somewhat greater in the liquid fraction obtained with LDPE than HDPE (the yield of gases and liquids, and the composition of these fractions for other components being very similar in all other respects). When comparing these results to those found in the bibliography, not only do experimental conditions possibly play a role, but also the polymer structure or the presence of traces of some compounds

**Table 1**

Yields of the different fractions: gases, liquids-waxes and coke (expressed as mg/100 mg of polyethylene) obtained during the thermal and catalytic pyrolysis of LDPE and HDPE over HZSM5 and HUSY

Yield (mg/100 mg of polyethylene)	LDPE	HDPE	LDPE-HZSM5	HDPE-HZSM5	LDPE-HUSY	HDPE-HUSY
Gases	14.6	16.3	70.7	72.6	34.5	39.5
Liquids/waxes	93.1	84.7	18.3	17.3	61.6	41.0
Coke	–	–	0.5	0.7	1.9	1.9
Total yield	107.7	101.0	89.5	90.6	98.0	82.4

**Table 2**

Types of compounds (expressed as weight fraction) obtained in the gaseous and condensable fractions during the thermal and catalytic pyrolysis processes of LDPE and HDPE over HZSM5 and HUSY

Weight fraction (%)	LDPE	HDPE	LDPE-HZSM5	HDPE-HZSM5	LDPE-HUSY	HDPE-HUSY
Gases						
<i>n</i> -Paraffins	31.8	29.1	7.7	15.2	10.9	5.6
<i>iso</i> -Paraffins	2.1	1.9	9.0	11.7	23.7	16.8
1-Olefins	46.3	47.3	15.8	21.4	11.0	16.5
Olefins	19.5	21.5	67.3	51.4	53.6	61.0
Aromatics	0.3	0.2	0.2	0.3	0.8	0.1
Liquids/waxes						
<i>n</i> -Paraffins	33.4	37.0	4.4	3.8	23.4	7.5
<i>iso</i> -Paraffins	0.0	0.0	4.1	2.9	11.4	30.4
1-Olefins	51.0	44.0	8.6	18.7	16.4	6.0
Olefins	15.6	19.0	30.8	24.0	17.5	12.3
Aromatics	0.0	0.0	52.1	50.6	31.3	43.8

from the polymerization process. Williams and Williams [17] and Ballice et al. [14], working under dynamic conditions similar to those used in this study, also reported only very small differences between the products evolved from both types of polyethylene. Williams and Williams [17] found somewhat more olefins in the gases obtained from HDPE whilst, according to Ballice et al. [14], the yield of gases is somewhat greater in the pyrolysis of HDPE than LDPE. Escola [18] also reported a higher yield in gases for HDPE than LDPE in a batch reactor under isothermal conditions (400 °C). Conesa et al. [19] observed more olefins in the gases obtained from HDPE than LDPE in a fluidized bed reactor at 800 °C, to the detriment of aromatics. It is worth mentioning here that only a few studies refer to the appreciable amount of aromatics generated in the thermal pyrolysis of polyethylene, as is the case of Conesa et al. [19], who found 18.4% aromatics in a fluidized bed reactor at 800 °C, and Park et al. [20], who found 19.1% aromatics in a batch reactor at 450 °C.

### 3.1.2. Catalytic pyrolysis

Table 1 shows that the quantity of gases generated drastically increases when the catalysts are employed, especially in mixtures with HZSM5, whilst liquids/waxes and coke deposits are more abundant with the HUSY zeolite than with HZSM5. This behaviour can be justified by considering the structure and acidity of these catalysts. HZSM5 is characterized by a relatively small pore size, surface area and high number of both, weak and strong acid sites. Whether the polymer molecules or their primarily generated fragments, react first on the surface of the catalyst or, they or the chain ends or long branches are able to penetrate into the pores, is a topic of controversy. Manos et al. [21] and Lin et al. [6] stated that large macromolecules have to react on the external surface of the zeolite first, whilst Aguado et al. [22] observed that the external surface of HZSM5 crystals plays a negligible role in the cracking of polyethylene. On the other hand, Zhou et al. [23] confirmed that polyethylene molecules were able to diffuse into the narrow pores of modified HZSM5, whilst other polymers like polypropylene were not. Accordingly, Marcilla et al. [24,25] suggested that the polymer branches or chain ends of polyethylene may penetrate into the zeolite pores, reaching the acid sites located there, thus increasing activity. Furthermore, HZSM5 possesses strong and weak acid sites, whereas HUSY only has weak ones, and strong acid sites are more effective in catalyzing the degradation and/or cracking of heavier hydrocarbons into lighter compounds than weak acid sites [26]. On the other hand, since the surface area and pore size of HUSY are bigger than those of HZSM5, reactions on the surface and in the pores should be favoured when using this zeolite. Nevertheless, the large cavities of HUSY permit the

formation of bulky coke precursors, leading to a fast deactivation of the catalyst [20]. Moreover, the relatively weak acid sites of HUSY are not as effective in promoting the cracking process.

Hernández et al. [10] carried out the catalytic pyrolysis of HDPE over HZSM5 and HUSY (20% by weight) in a fluidized bed reactor at 500, 600, 700 and 800 °C. At the lowest temperature, and in the presence of HZSM5, the yield of gases, liquids, waxes and solid residue was 88.3, 4.3, 5.0 and 5.6 wt%, respectively. In the presence of HUSY, the proportion of gases is substantially greater than described in this study: the percentages by weight of each fraction were 83.4, 9.7, 1.0 and 10.9, respectively. Garforth et al. [27] also studied the catalytic degradation of HDPE in a fluidized bed reactor using HZSM5 and HUSY, and obtained very similar results to those of Hernández et al. [10]. At 430 °C, and in the presence of HZSM5 (40 wt%), the yield of gases, liquids and residue was 95.4, 1.6 and 3.0 wt%, respectively. Whilst with HUSY, 93.4, 1.4 and 5.2 wt% gases, liquids and residue were obtained. These authors reported a very high yield for gases in the presence of HUSY zeolite, if compared to results shown in Table 1, and their experimental conditions differed drastically from those employed in this study (the type of reactor and proportion of catalyst). Such differences are less marked when results are compared to those of authors that used a batch reactor. Seo et al. [15] compared the catalytic degradation of HDPE over HZSM5 and HY in a batch reactor at 450 °C (isothermal conditions). With HZSM5, 63.5 wt% of gases, 35.0 wt% of liquids, and 1.5 wt% of coke were obtained. While the yield of gases, liquids and coke was 27.0, 71.5 and 1.5 wt% with HY. A similar study was carried out by Uemichi et al. [28], for the catalytic cracking of LDPE over HZSM5 and HY. The process using HZSM5 yielded 67.5, 31.1 and 1.4 wt% gas, liquid and coke; whilst 58.5 wt% gases, 24.3 wt% liquids, 2.8 wt% waxes and 14.4 wt% coke were obtained using HY. Unlike the results showed in Table 1, the material balance achieved by these last authors is 100% because the yield of gas was calculated by difference.

When the yield of gases, liquids/waxes and coke for both polyethylenes undergoing the catalytic processes are compared, similarities in behaviour are evident. However, when the yields of the various groups of compounds within each fraction are analyzed, appreciable differences can be found depending on the type of catalyst, and also on the type of polymer. Table 2 shows the weight percentage of the various groups of compounds found in the gas and liquid/wax fractions. In the presence of HZSM5, olefins were the major compounds in gases, especially for LDPE. 1-Olefins, *n*-paraffins and *iso*-paraffins also show appreciable yields, whilst only a very small amount of aromatics was found. Nevertheless, in the liquids/waxes fraction aromatics were by far the major compounds.

Hesse et al. [29] analyzed the composition of the gases obtained from the catalytic pyrolysis of polyethylene (type not specified) over HZSM5 in a batch reactor, and from dynamic experiments similar to those carried out in this study. They found 60.3% olefins, 24.2% *n*-paraffins and 15.5% aromatics, whilst we found 83.1% (olefins + 1-olefins), 16.7% (*n*-paraffins + *iso*-paraffins) and 0.2% aromatics for LDPE-HZSM5, and 72.8, 26.9 and 0.3%, respectively for HDPE-HZSM5. It has to be stated that Hesse et al. [29] did not mention the presence of any condensed fraction, which under the experimental conditions employed could have undergone secondary reactions. When the weight fraction of every group of compounds in both the gaseous and condensed fractions is considered, many similar results are obtained. For LDPE-HZSM5, 74.1% olefins, 15.1% paraffins and 10.8% aromatics are produced. Similarly, 67.1, 23.0 and 9.9%, are generated for HDPE-HZSM5, respectively. Park et al. [20] also carried out the catalytic pyrolysis of HDPE in a fixed bed reactor, obtaining for the liquid fraction 50.7% aromatics and 20.0% olefins, results that are very similar to those presented here. On the other hand, Mastral et al. [30] studied

the degradation of HDPE over *n*-HZSM5 in a fluidized bed reactor at 500 °C and also obtained gases rich in olefins, but the wax composition was different to that shown in this paper: 53.0% paraffins, 45.0% olefins and 2.0% aromatics. Nevertheless, Hernández et al. [10] working under similar conditions to those of Mastral et al. [30] in a fluidized bed reactor obtained similar results to those indicated in our study and the liquid fraction was composed of 15.8% paraffins, 15.8% olefins and 68.4% aromatics.

The high percentage of aromatics obtained with the HZSM5 zeolite could be explained by the high number of Brønsted acid sites contained within this zeolite, where aromatization reactions are favoured [20]. A high yield of olefins is expected using this sort of catalyst, since bimolecular reactions conducive to the production of saturated compounds are sterically hindered by the small pore size [31]. Moreover, HZSM5 is hydrophobic, and thus exhibits a weak adsorption of polar molecules [32].

As with the results obtained for HZSM5, olefins are the major compounds in gases generated using the HUSY zeolite, and appreciable quantities of iso-paraffins, 1-olefins and *n*-paraffins are produced. In the condensed fraction, great differences were found depending on the polyethylene type. In the LDPE-HUSY and HDPE-HUSY systems, the major compounds were aromatics, followed by *n*-paraffins and olefins in the first case, and iso-paraffins and olefins in the latter. A glance at the bibliography shows a high divergence in the results obtained for these systems by other authors. In the study by Hesse et al. [29] mentioned earlier, which was carried out in a batch reactor, the gases obtained with the HY zeolite were composed of 83.3% paraffins, 14.2% olefins and 2.6% aromatics, showing marked differences from the results presented here (34.6, 64.6 and 0.8% for paraffins, olefins and aromatics for the LDPE-HUSY system, and 22.4, 77.5 and 0.1% for HDPE-HUSY). Hernández et al. [9] studied the HDPE-HUSY system in a fluidized bed reactor, and despite the differences in experimental conditions, their results match those presented here rather well. It is worth mentioning that these authors employed the same commercial polymer and zeolites as those used for the present study. For example, at 500 °C, the gases obtained by Hernández et al. [9] were composed of 24.8% paraffins, 72.5% olefins and 2.7% aromatics, whilst the condensed fraction [10] was composed of 59.7% aromatics, 36.6% paraffins and 3.7% olefins, comparable to the 43.8, 37.9 and 18.3% obtained for the condensed fraction in our study. On the other hand, the results obtained by Elordi et al. [33] in a conical spouted bed reactor were also similar to those shown in this study. Thus, the composition of condensable fraction resulting

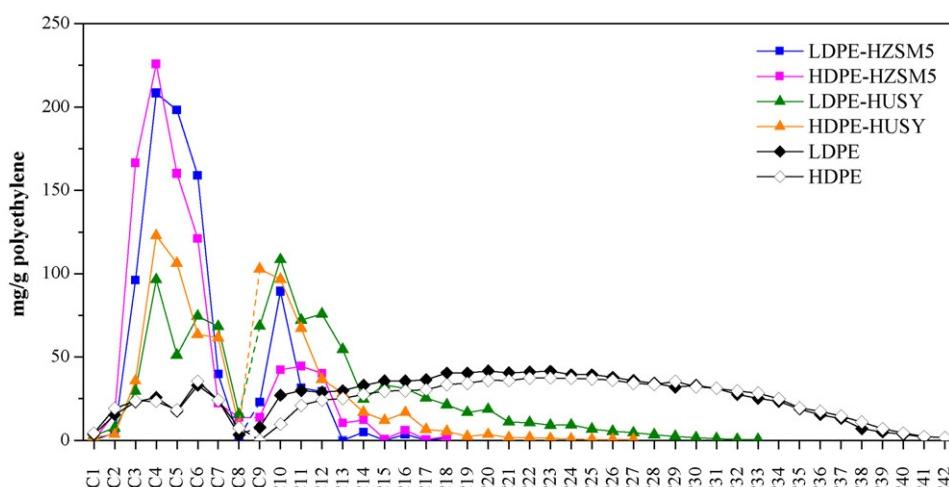
of catalytic pyrolysis of HDPE with HY was 33.80% aromatics, 43.64% paraffins and 15.68% olefins. On the other hand, Park et al. [20] obtained 29.4% aromatics, 39.7% paraffins and 23.0% olefins as the composition of the condensed fraction using the HY zeolite in a fixed bed reactor.

Comparing results obtained using the two catalysts, the weight fraction of iso-paraffins is greater in the condensed fraction, whilst the proportion of olefins is found to decrease, when HUSY is used instead of HZSM5. During aromatization reactions, a considerable number of hydrogen atoms are abstracted which subsequently accumulate on the catalyst's surface, and can then be consumed in the hydrogenation of olefins [15,34]. Moreover, as opposed to HZSM5, HUSY adsorbs polar molecules strongly, which may also lead to a possible explanation for the increase of iso-paraffins to the detriment of olefins.

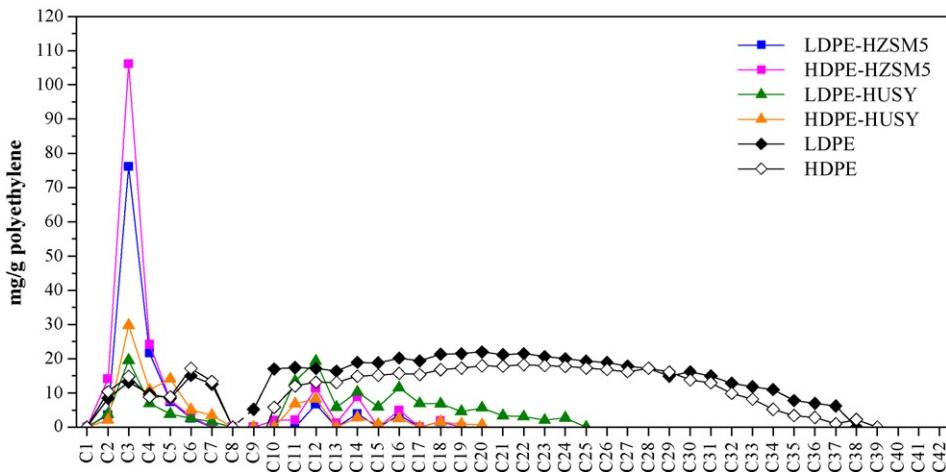
### 3.2. Carbon number distribution of the products evolved from the thermal and catalytic pyrolysis

Fig. 2 shows the distribution of the number of carbon atoms for the thermal and catalytic experiments carried out. In all cases there is a discontinuity at compounds with C8 and C9, which coincides with the change in the method of analysis (GC-FID was used to identify low molecular weight compounds and GC-MS for compounds from C9). The peak corresponding to these compounds could be overlapping with that of the solvent (*n*-hexane) in the GC-MS column. Consequently, the yields obtained for these compounds may be lower than actual yields. The lack of success in quantifying compounds from C5 to C9 has also been described by other authors that carried out similar experiments [20,34].

As is known, the thermal pyrolysis of polyethylene causes the polymer backbone to break and form hydrocarbon radicals, which may contain any number of carbon atoms. It is for this reason that the hydrocarbons generated exhibit wide chain length distributions [11,26]. In fact, Fig. 2 shows a wide and even distribution of carbon atoms from C1 to C42 for the thermal processes. Products obtained during the catalytic processes exhibit a narrower distribution: C1 to C13 for LDPE-HZSM5, C1 to C15 for HDPE-HZSM5, C1 to C29 for LDPE-HUSY and C1 to C19 for HDPE-HUSY. The maximum yield also shifts to compounds of low molecular weight. The carbon number distribution is narrower for HZSM5 than HUSY, which might, as commented before, be due to the acidity and structural characteristics of both catalysts [15,27,32]. Moreover, it can be seen for HZSM5 that the carbon number



**Fig. 2.** Distribution of the number of carbon atoms for the products obtained during the thermal and catalytic processes.



**Fig. 3.** Distribution of the number of carbon atoms obtained for 1-olefins during the thermal and catalytic processes.

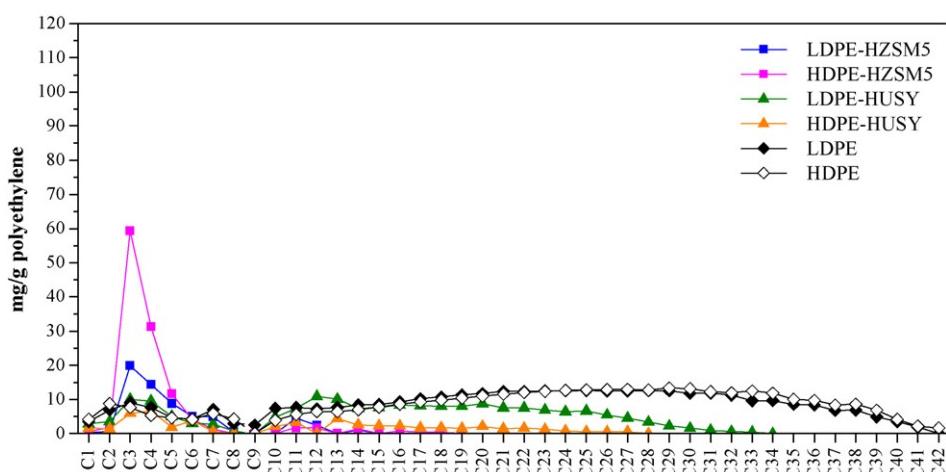
distribution is independent of the type of polyethylene used, which coincides with results obtained by Aguado et al. [22]. On the contrary, when the zeolite HUSY is employed, the distribution of products obtained for LDPE is wider than for HDPE. On the other hand, and in contrast with the thermal processes, compounds of a certain chain length are favoured over others in catalytic processes. With HZSM5, major compound carbon numbers range from C3 to C6, since chain scission takes place from the chain ends within the pores of this catalyst [22]. These results are in accordance with those of other authors [26,34–36]. In the case of HUSY, the major compounds have carbon numbers ranging from C4 to C12. Other authors obtained similar results [27,32,37,38].

Figs. 3–8 show carbon number distribution grouped by compound type: 1-olefins (Fig. 3), *n*-paraffins (Fig. 4), olefins (Fig. 5), iso-paraffins (Fig. 6), aromatics (Fig. 7) and diolefins (Fig. 8). The carbon number distribution obtained for the major compounds of the thermal processes (1-olefins and *n*-paraffins) is very regular, and continues up to long chains, reaching up to C42 for *n*-paraffins and up to C39 for 1-olefins. With the catalysts, the shape of the curve differs from the symmetrical distribution seen for the thermal processes, and shifts to compounds of lower molecular weight. For HZSM5, the maximum number of carbon atoms for 1-olefins is 19, and the high yield of propene is worth noting (Fig. 3). For HUSY, on the other hand, olefins with up to 25 carbon atoms were found to be present. The *n*-paraffins (Fig. 4) exhibit very

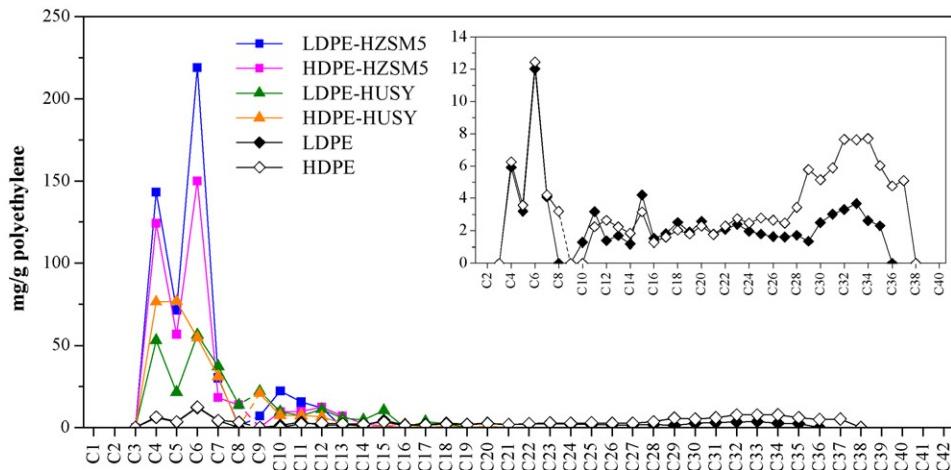
similar behaviour to the 1-olefins: very large amounts of propane and *n*-butane yield with the zeolite HZSM5, especially when used in conjunction with HDPE; and larger distributions of carbon atoms also occur for HUSY than for HZSM5.

Fig. 5 shows the carbon atom distribution for olefins which, as shown in Table 2, are by far the major components of the gases obtained during the catalytic processes. The maximum in the carbon atom distribution is centred for both catalysts on molecules from C4 to C6, with yields exceeding 100 mg g<sup>-1</sup> of polyethylene in experiments with HZSM5 for some of these compounds. No olefins with more than 20 carbon atoms formed during the catalytic processes. Rather small quantities of olefins formed during the thermal processes, so the scale showing variation across carbon number has been stretched to improve representation. The distribution obtained for these compounds during the thermal processes exhibits peculiar behaviour since, in contrast to 1-olefins and *n*-paraffins, it is not regular at all and has a maximum for low molecular weight compounds (C4 to C7) and, another for high molecular weight compounds (C28 to C37).

The carbon number distribution for iso-paraffins is shown in Fig. 6. With HZSM5, only the yields of iso-paraffins with low molecular weights (C4 to C6) are marked, whereas the yields of these compounds with HUSY are greater, and iso-paraffins up to C19 may be encountered. For the thermal processes, the yields for these compounds are not appreciable. The corresponding dis-



**Fig. 4.** Distribution of the number of carbon atoms obtained for *n*-paraffins during the thermal and catalytic processes.



**Fig. 5.** Distribution of the number of carbon atoms obtained for olefins during the thermal and catalytic processes.

tribution for aromatics is shown in Fig. 7. Aromatics from C9 to C13 are formed during the catalytic processes, the highest yields being achieved using HUSY. Fig. 8 shows the distribution for diolefins. These compounds show a regular, though narrower, distribution ranging from C9 to C32 for the thermal processes, compared to the other compounds. For the catalytic processes, only the yield obtained for the LDPE-HUSY system deserves notice.

### 3.3. Yield for the main compounds obtained

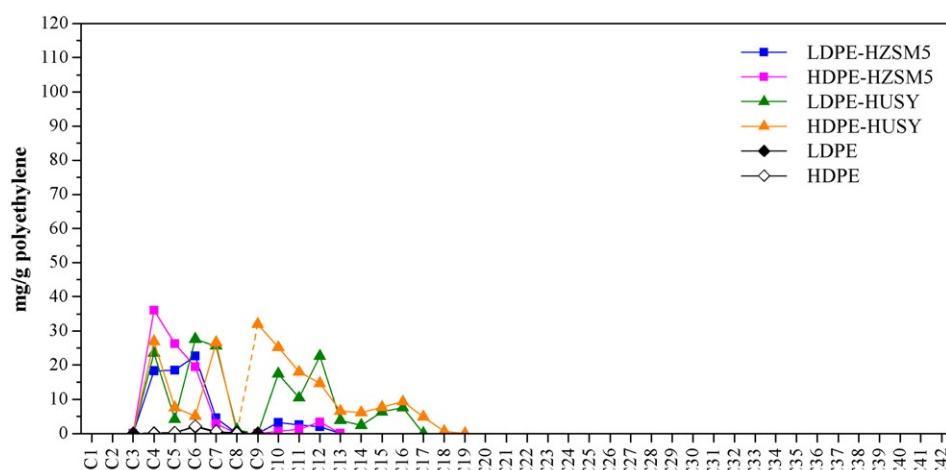
Table 3 shows the yields of the 10 major compounds in each experiment. For the thermal processes, all the major compounds are 1-olefins with 16–28 carbon atoms, except for 1-hexene, which is formed during the HDPE degradation. Yields are very similar for all these compounds, and no significant differences exist between the two polyethylenes.

However, when the catalysts are used, the yields of the major compounds change drastically. With HZSM5, the yields of propene, 2-methyl-2-butene and isobutene are very high. For the LDPE-HZSM5 system, the major compound is 2-methyl-2-butene with a yield of  $91.6 \text{ mg g}^{-1}$  of polyethylene, followed by isobutene and propene ( $77.9$  and  $76.0 \text{ mg g}^{-1}$  of polyethylene, respectively). For the HDPE-HZSM5 system, the high yield of propene ( $106.1 \text{ mg g}^{-1}$  of polyethylene) is remarkable, as are some of the lower yields for isobutene, propane and 2-methyl-2-butene. The other major

compounds obtained with HZSM5 always have low molecular weights (olefins, linear and branched paraffins with 4–6 carbon atoms).

A large variety of compounds were obtained among the ten major compounds during the catalytic processes with HUSY: olefins, paraffins and aromatics, which, moreover, presented higher molecular weights than with the catalyst HZSM5 (C3 to C12 for HUSY and C3 to C6 for HZSM5). The yield achieved for the major compounds is in this case  $37.3 \text{ mg g}^{-1}$  of polyethylene (*2-cis*-butene in the HDPE-HUSY system), which is quite low compared to the yields obtained with HZSM5 for the major compounds. The major compounds for both polyethylenes were *2-cis*-butene, propene, isoprene and isobutane, in that order, and all of them yielded in comparable amounts, as in the case of the thermal processes.

Consequently, only in the case of HZSM5 is a high selectivity for compounds with interesting industrial applications (such as propene, 2-methyl-2-butene, isobutene and propane) found when comparing the two catalysts. In general, light olefins (with no more than 5 carbon atoms) increase the quality of gasoline by increasing the gasoline octane number [39]. Isobutene is a very good alkylating agent of paraffins, thus enabling preparation of branched hydrocarbons as valuable blends for engine fuels. The alkylating potency of butenes may be capitalised on in the preparation of specialty chemicals, e.g. polymer antidegradants, polycyclic aromatic acid precur-



**Fig. 6.** Distribution of the number of carbon atoms obtained for iso-paraffins during the thermal and catalytic processes.

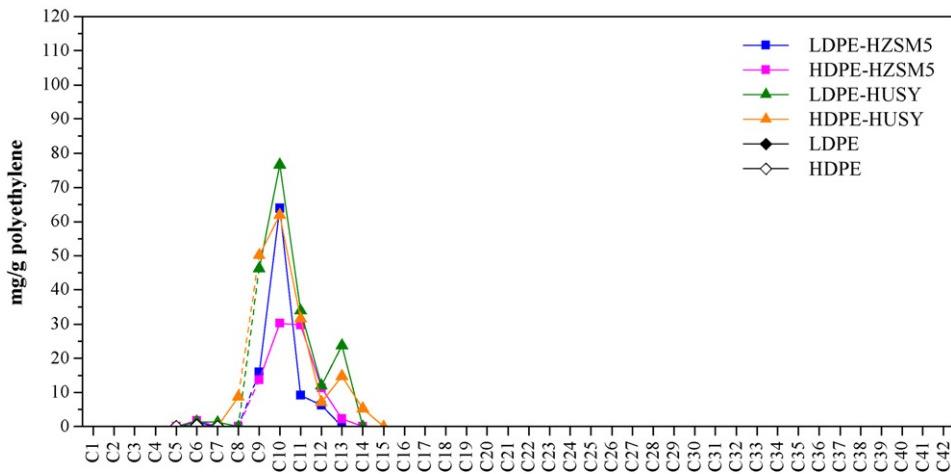


Fig. 7. Distribution of the number of carbon atoms obtained for aromatics during the thermal and catalytic processes.

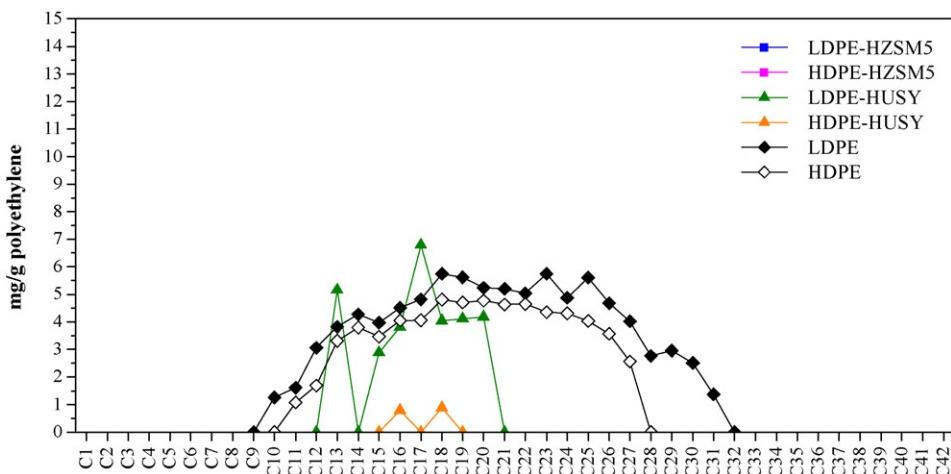


Fig. 8. Distribution of the number of carbon atoms obtained for diolefins during the thermal and catalytic processes.

sors, etc. Not less important is the application of isobutene to polymer chemistry, either directly as a monomer, or as an intermediate in the production of methacrylic acid [40]. The demand for propene is increasing rapidly due to the expanding market for polypropylene and LPG-range olefins used as feedstock for alkylation and isomerization units, in which clean, high octane

gasoline components and other chemicals (such as phenol, acetone, butylic alcohols) are produced [39,41]. Propane finds use as a cooling agent, liquefied gas for domestic purposes, and solvent in asphalt removal processes [42].

Although the yields of particular aromatic compounds from the catalytic processes are not very great, high global yields of

Table 3

Yields of the 10 major compounds (expressed as mg/g of polyethylene) obtained during the thermal and catalytic pyrolysis of LDPE and HDPE over HZSM5 and HUSY

Compound	mg/g PE	HDPE		LDPE-HZSM5		HDPE-HZSM5		LDPE-HUSY		HDPE-HUSY	
		Compound	mg/g PE	Compound	mg/g PE	Compound	mg/g PE	Compound	mg/g PE	Compound	mg/g PE
1-Olefin C20	22.0	1-Olefin C22	18.3	2-Methyl-2-butene	91.6	Propene	106.1	2-cis-Butene	30.9	2-cis-Butene	37.3
1-Olefin C19	21.5	1-Olefin C23	18.0	Isobutene	77.9	Isobutene	65.1	Isobutane	23.5	Propene	29.7
1-Olefin C22	21.5	1-Olefin C20	17.9	Propene	76.0	Propane	59.4	2-Methylpentane	22.9	Isoprene	27.5
1-Olefin C18	21.3	1-Olefin C21	17.9	4-Methyl-2-cis-pentene	44.8	2-Methyl-2-butene	57.5	Trimethylbenzene	21.8	Isobutane	26.9
1-Olefin C21	21.2	1-Olefin C24	17.7	2-trans-Butene	40.9	2-trans-Butene	38.8	Propene	19.5	2-trans-Pentene	26.8
1-Olefin C23	20.6	1-Olefin C19	17.3	2-cis-Pentene	38.6	Isobutane	36.1	1-Olefin C12	19.3	Isobutene	23.9
1-Olefin C16	20.2	1-Olefin C25	17.3	2-trans-Pentene	27.5	4-Methyl-2-cis-pentene	31.6	2-Methyl-2-butene	16.6	2-trans-Butene	15.4
1-Olefin C24	20.0	1-Hexene	17.2	2-cis-Butene	24.3	n-Butane	31.4	1-Methylpropylbenzene	14.4	3-Methyl-1-butene	14.7
1-Olefin C17	19.4	1-Olefin C28	17.2	1-Butene	21.7	2-cis-Pentene	30.2	1-Olefin C11	13.4	1-Pentene	14.1
1-Olefin C25	19.3	1-Olefin C26	16.9	Propane	19.9	Isopentane	25.2	Isobutene	13.1	Trimethylbenzene	13.8

aromatics were obtained, especially with the HUSY zeolite: 96.5 mg g<sup>-1</sup> of polyethylene for LDPE-HZSM5, 89.2 mg g<sup>-1</sup> of polyethylene for HDPE-HZSM5, 195.3 mg g<sup>-1</sup> of polyethylene for LDPE-HUSY and 180.3 mg g<sup>-1</sup> of polyethylene for HDPE-HUSY. This fact is important because aromatics are key contributors to a higher gasoline octane number that, in turn, improves the gasoline's quality [43].

#### 4. Conclusions

1. The thermal pyrolysis of polyethylene under dynamic conditions yields higher quantities of liquids than gases, and both fractions are mainly composed of 1-olefins and *n*-paraffins. Small quantities of olefins, and some *iso*-paraffins and aromatics are also obtained. The results of most studies in the bibliography support those presented here, but studies carried out at low temperatures report a higher proportion of *n*-paraffins than 1-olefins.
2. During the thermal processes, the two polyethylenes exhibit similar behaviour. However, a higher proportion of 1-olefins form during the pyrolysis of LDPE. Some authors report a higher proportion of gases for HDPE than LDPE.
3. The carbon number distribution obtained during the thermal processes is wide (from C1 to C42), even for 1-olefins and *n*-paraffins, but exhibits peculiar behaviour for olefins, having a maximum for low (C4 to C7), and another for high molecular weight olefins (C28 to C37).
4. For the thermal processes, the 10 major compounds are 1-olefins having 16–28 carbon atoms, and all of them yield in very similar amounts.
5. The amount of gases generated drastically increases when catalysts are employed, especially with HZSM5, whilst liquids and the coke deposit are more abundant with HUSY. This peculiarity can be rationalized by looking at the structure and acidity of the catalysts. These results agree strongly for those authors working in batch processes, whilst authors employing a fluidized bed found that higher amounts of gases were generated, especially with HUSY.
6. For the HZSM5 zeolite, olefins are the major compounds in the gas fraction, followed by 1-olefins, *n*-paraffins and *iso*-paraffins, whilst in the liquid fraction, aromatics are by far the major compounds. Similarly, for gases generated in the presence of HUSY, olefins are the major compounds, whilst also appreciable quantities of *iso*-paraffins, 1-olefins and *n*-paraffins are obtained. The composition of the liquid fraction formed using this zeolite depends largely on the type of polyethylene employed. The major compounds are aromatics, followed by *n*-paraffins and olefins in the LDPE-HUSY system, and *iso*-paraffins and olefins in the HDPE-HUSY system. When catalysts are used, the differences observed by the various authors seem to have more to do with the characteristics of the polymer and the zeolite, than with the experimental conditions.
7. The carbon number distribution for the catalytic processes is narrower, especially for HZSM5: from C1 to C13 for LDPE-HZSM5, C1 to C15 for HDPE-HZSM5, C1 to C29 for LDPE-HUSY and C1 to C19 for HDPE-HUSY, and, in contrast with the thermal processes, the maximum yield is not centred, it shifts to compounds from C3 to C6 for HZSM5 and C4 to C12 for HUSY.
8. With the HZSM5 zeolite, the high yields achieved for propene, 2-methyl-2-butene and isobutene are remarkable. All these compounds have interesting industrial applications. For example, the yield of propene is as large as 106.1 mg g<sup>-1</sup> of polyethylene for the HDPE-HZSM5 system. For HUSY, the major compounds were 2-*cis*-butene, propene, isoprene and isobutane, formed in substantially lower yields than with HZSM5.

#### Acknowledgements

Financial support for this investigation has been provided by the Spanish “Comisión de Investigación Científica y Tecnológica” de la Secretaría de Estado de Educación, Universidades, Investigación y Desarrollo and the European Community (FEDER refunds) (CICYT CTQ2004-02187), by the Generalitat Valenciana (project ACOMP/2007/094), and by University of Alicante, Grupo de Procesado y Pirólisis de Polímeros (VIGROB099).

#### References

- [1] Association of Plastics Manufacturers in Europe (APME), PlasticsEurope, An Analysis of Plastics Consumption and Recovery in Europe 2002 & 2003, Association of Plastics Manufacturers in Europe (APME), Brussels, 2004, pp. 1–18.
- [2] L.A. Wall, S.L. Madorsky, D.W. Brown, S. Straus, R. Simha, J. Am. Chem. Soc. 76 (1954) 3430–3437.
- [3] R. Simha, L.A. Wall, J. Bram, J. Chem. Phys. 29 (1958) 894–904.
- [4] H. Bockhorn, A. Hornung, U. Hornung, D. Schawaller, J. Anal. Appl. Pyrol. 48 (1999) 93–109.
- [5] A.G. Buekens, H. Huang, Resource Conserv. Recycl. 23 (1998) 163–181.
- [6] Y.H. Lin, W.H. Hwu, M.D. Ger, T.F. Yeh, J. Dwyer, J. Mol. Catal. A: Chem. 171 (2001) 143–151.
- [7] B.W. Wojciechowski, A. Corma, Catalytic Cracking. Catalysts, Chemistry, and Kinetics, Chemical Industries, vol. 25, Marcel Dekker, Inc., New York, 1986.
- [8] A. Corma, Chem. Rev. 95 (1995) 559–614.
- [9] M.R. Hernández, A.N. García, A. Marcilla, J. Anal. Appl. Pyrol. 73 (2005) 314–322.
- [10] M.R. Hernández, A.N. García, A. Marcilla, J. Anal. Appl. Pyrol. 78 (2007) 272–281.
- [11] P.T. Williams, E.A. Williams, J. Anal. Appl. Pyrol. 51 (1999) 107–126.
- [12] M. Predel, W. Kaminsky, Polym. Degrad. Stab. 70 (2000) 373–385.
- [13] Y. Liu, J. Qian, J. Wang, Fuel Process. Technol. 63 (2000) 45–55.
- [14] L. Balice, M. Yuksel, M. Saglam, R. Reimert, H. Schulz, Energy Fuels 12 (1998) 925–928.
- [15] Y.H. Seo, K.H. Lee, D.H. Shin, J. Anal. Appl. Pyrol. 70 (2003) 383–398.
- [16] J. Aguado, D.P. Serrano, G. San Miguel, M.C. Castro, S. Madrid, J. Anal. Appl. Pyrol. 79 (2007) 415–423.
- [17] E.A. Williams, P.T. Williams, J. Chem. Technol. Biotechnol. 70 (1997) 9–20.
- [18] J.M. Escola, Ph.D. Thesis, Universidad Complutense de Madrid, 1998.
- [19] J.A. Conesa, R. Font, A. Marcilla, Energy Fuels 11 (1997) 126–136.
- [20] D.W. Park, E.Y. Hwang, J.R. Kim, J.K. Choi, Y.A. Kim, H.C. Woo, Polym. Degrad. Stab. 65 (1999) 193–198.
- [21] G. Manos, A. Garforth, J. Dwyer, Ind. Eng. Chem. Res. 39 (2000) 1203–1208.
- [22] J. Aguado, J.L. Sotelo, D.P. Serrano, J.A. Calles, J.M. Escola, Energy Fuels 11 (1997) 1225–1231.
- [23] Q. Zhou, L. Zheng, Y.Z. Wang, G.M. Zhao, B. Wang, Polym. Degrad. Stab. 84 (2004) 493–497.
- [24] A. Marcilla, A. Gómez, A.N. García, M.M. Olaya, J. Anal. Appl. Pyrol. 64 (2002) 85–101.
- [25] A. Marcilla, M.I. Beltrán, F. Hernández, R. Navarro, Appl. Catal. A: Gen. 278 (2004) 37–43.
- [26] Y. Sakata, M.A. Uddin, A. Muto, J. Anal. Appl. Pyrol. 51 (1999) 135–155.
- [27] A.A. Garforth, Y.H. Lin, P.N. Sharratt, J. Dwyer, Appl. Catal. A: Gen. 169 (1998) 331–342.
- [28] Y. Uemichi, M. Hattori, T. Itoh, J. Nakamura, M. Sugioka, Ind. Eng. Chem. Res. 37 (1998) 867–872.
- [29] N.D. Hesse, R. Lin, E. Bonnet, J. Cooper, R.L. White, J. Appl. Polym. Sci. 82 (2001) 3118–3125.
- [30] J.F. Mastral, C. Berreueco, M. Gea, J. Ceamanos, Polym. Degrad. Stab. 91 (2006) 3330–3338.
- [31] P.N. Sharratt, Y.H. Lin, A.A. Garforth, J. Dwyer, Ind. Eng. Chem. Res. 36 (1997) 5118–5124.
- [32] G. Manos, A. Garforth, J. Dwyer, Ind. Eng. Chem. Res. 39 (2000) 1198–1202.
- [33] G. Elordi, M. Olazar, R. Aguado, G. Lopez, M. Arabiurrutia, J. Bilbao, J. Anal. Appl. Pyrol. 79 (2007) 450–455.
- [34] H. Ohkita, R. Nishiyama, Y. Tochihara, T. Mizushima, N. Kakuta, Y. Morioka, A. Ueno, Y. Namiki, S. Tanifuiji, H. Katoh, H. Sunazuka, R. Nakayama, T. Kuroyanagi, Ind. Eng. Chem. Res. 32 (1993) 3112–3116.
- [35] K. Takuma, Y. Uemichi, A. Ayame, Appl. Catal. A: Gen. 192 (2000) 273–280.
- [36] N. Miskolczi, L. Bartha, G. Deak, B. Jover, D. Kallo, J. Anal. Appl. Pyrol. 72 (2004) 235–242.
- [37] Y.H. Lin, P.N. Sharratt, A.A. Garforth, J. Dwyer, Energy Fuels 12 (1998) 767–774.
- [38] R. Bagri, P.T. Williams, J. Anal. Appl. Pyrol. 63 (2002) 29–41.
- [39] M.A. den Hollander, M. Wissink, M. Makkee, J.A. Moulijn, Appl. Catal. A: Gen. 223 (2002) 85–102.
- [40] V. Macho, M. Kralik, E. Jurecekova, J. Hudec, L. Jurecek, Appl. Catal. A: Gen. 214 (2001) 251–257.
- [41] O. Bortnovsky, P. Sazama, B. Wichterlova, Appl. Catal. A: Gen. 287 (2005) 203–213.
- [42] V. Érij, M. Rásina, M. Rudin, Química y Tecnología del Petróleo y del Gas, MIR Moscú, Moscú, 1988, p. 297.
- [43] J. Scheirs, W. Kaminsky, Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels, John Wiley & Sons, Ltd., Chichester, United Kingdom, 2006, pp. 249–362.